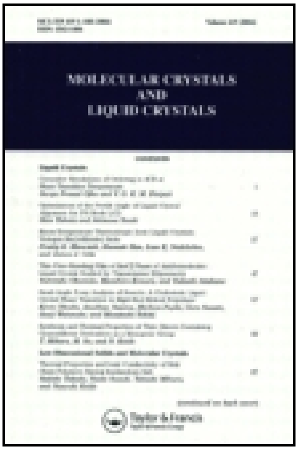

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Fluoro- and Nitro-Substitution Effect of Some Chiral Compounds

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Fluoro- and Nitro-Substitution Effect of Some Chiral Compounds

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Four chiral compounds have been synthesized. Their phase transition behavior was investigated by differential scanning calorimetry and polarized optical microscopy. Two of them show monotropic smectic C phases. Moreover, one of them shows an enantiotropic blue phase. The lateral fluoro-substitution strongly suppressed the formation of SmC* phases and decreased clearing points. Although the introduction of nitro group in the core decreased the length-diameter ratio, the temperature range of monotropic SmC* phase did not change much.*

Keywords: chiral; fluoro; liquid crystal

INTRODUCTION

Liquid crystals with smectic C* (SmC*) phases attracted many researchers, which are suitable to be applied in ferroelectric liquid crystal displays (FLCD) [1–13]. Because liquid crystals with fluoro-substituents show low viscosity, low conductivity, and high chemical and thermostability, many liquid crystals with fluoro-substituents both in the cores and alkoxy chains were designed and synthesized [7–15]. Moreover, chiral compounds with donors and acceptors are also attractive because they can be used as second-order nonlinear optical materials [16]. For the preparation of multifunctional materials which can potentially be applied in FLCD, second-order nonlinear optics, and photorefractive materials, one series of chiral liquid crystals with

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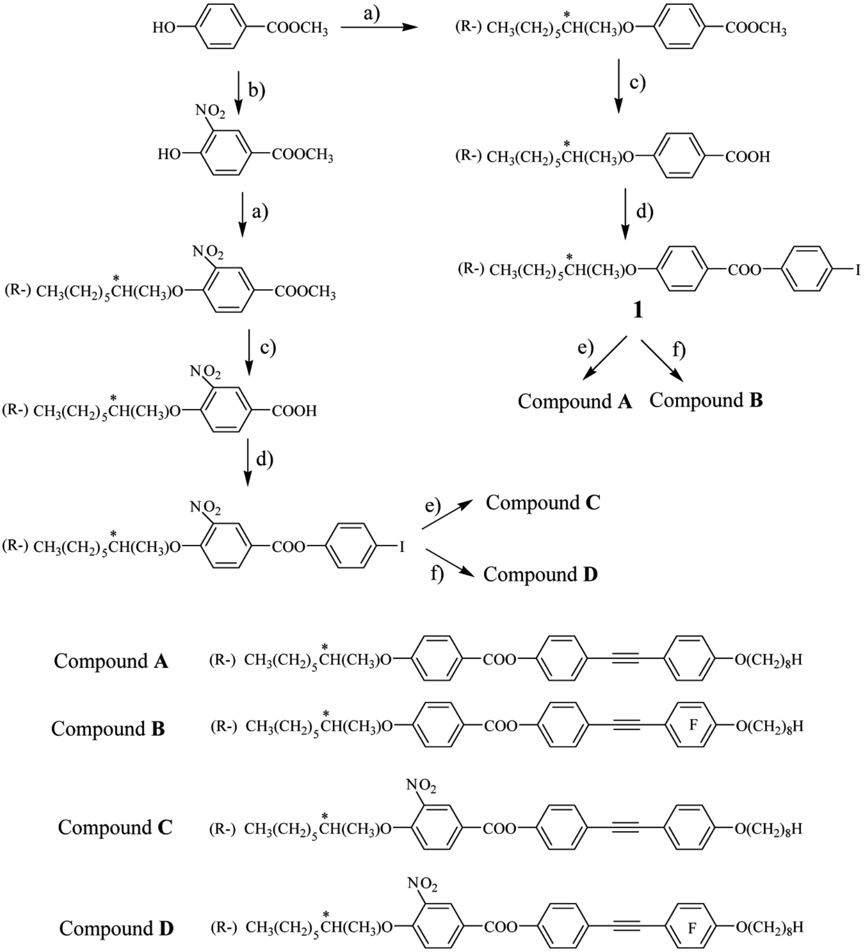

SCHEME 1 Synthesis of compounds **A**, **B**, **C**, and **D**. a) (S-) CH_3 $(CH_2)_5$ $C^*H(CH_3)OH$, DEAD/PPh_3, THF; b) HNO_3; c) 1) NaOH aq., EtOH 2) HCl aq.; d) *p*-I-phenol/DCC/DMAP, THF; e) 4-*n*-octoxyphenylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, THF/Et_3N; f) 4-*n*-octoxytetrafluorophenylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, THF/Et_3N.

nitro, fluoro, and (S-) 2-methylbutoxy groups were synthesized [17] with molecular structures that are similar to those shown in the Scheme. Generally, they show only the cholesteric (Ch) phase. The fluoro- and nitro-substitution effect was preliminary studied. Both fluoro- and nitro-substituents suppress the formation of liquid crystalline phases. Herein, the (R-) 1-methylheptoxy group was used as the

TABLE 1 Transition Temperatures of Compounds **A**, **B**, **C**, and **D**

A	Cr 52.2 Ch 127.5 I 127.5 Ch 48.5 SmC* 34.8 Recr
B	Cr 25.0 Ch 42.5 I 41.2 Ch 3.0 Recr
C	Cr 77.6 Ch 88.0 BP 88.5 I 88.5 BP 88.0 Ch 57.6 SmC* 40.7 Recr
D	liquid at r.t.

Cr = crystal; Ch = cholesteric phase; SmC* = chiral smectic C phase; BP = Blue phase; I = isotropic liquid; Recr = recrystal.

chiral alkoxy one. Because it is longer than the (S-) 2-methylbutoxy group, the association of the alkoxy chains may induce the formation SmC* phase [18].

RESULTS AND DISCUSSION

The intermediates were synthesized according to literature methods [9,10]. Compounds **A**, **B**, **C**, and **D** were synthesized according to the scheme.

The phase transition behavior of the final compounds was summarized in the table and figure, which was determined with polarizing optical microscopy. Compound **A** shows an enantiotropic cholesteric phase and a monotropic SmC* phase. Compared with previous results [17], the lateral interactions among the hydrocarbon chains should play an important role on the formation of the SmC* phase. Compound **B**, with fluoro-substituents in the core, smectic phases were suppressed. It shows only an enantiotropic cholesteric phase. Moreover, the clearing point decreases by 85°C. The lateral fluoro-substitution may not only suppress the lateral–lateral interactions among the cores, but also decrease the length–diameter ratio of **B**. However, it is interesting to find that the melting point is 25°C. It may be suitable to use in the FLCD mixtures [19,20].

Compound **C** which is **A** with a nitro group in the core shows enantiotropic cholesteric and blue phases, as well as a monotropic SmC* phase. Although the nitro group decreases the length-diameter ratio, it increases the polarity of **C**. Therefore, the SmC* phase temperature range did not change much. Moreover, because the existence of the chiral unit and the nitro group, compound **C** may be applied in second order nonlinear optical materials. During the last several years, more researchers were focused on studying blue phases. In 2002, H. Kikuchi *et al.* reported that the temperature range of polymer-stabilized liquid crystal blue phases could reach 66°C [21]. Recently, Sumsung introduced blue phase LCD technology at Society for Information Display 2008 symposium. Compound **C** shows an enantiotropic blue phase with a temperature range of 0.5°C. After being mixed with polymers or grafted on polymer main chains, the obtained materials may show blue phase with broader temperature ranges, which may be useful as the candidate in blue phase LCD. Compared with **A**, the introduction of a nitro group and a fluoro-substituent, compound **D** is liquid at room temperature. Unfortunately, it is difficult to purify.

CONCLUSION

In summary, four chiral compounds have been synthesized. The lateral fluoro-substitution strongly suppressed the formation of SmC* phases and decreased clearing points. Although the introduction of a nitro group in the core decreased the length-diameter ratio, the monotropic SmC* phase temperature range did not change much. Moreover, a blue phase was identified.

EXPERIMENTAL

Characterization

The structures of the final products and intermediates were determined by a variety of spectral methods. IR spectra were taken on a PE-983G spectrophotometer, using KBr pellets of the solids, or films of liquids. ^{1}H NMR spectra, with TMS as internal NMR standard were recorded on a Varian EM 360L spectrometer (60 MHz) or a Fx-90Q (90 MHz) instrument; ^{19}F NMR spectra, with trifluoroacetic acid (TFA) as external standard, were recorded on a Varian EM 360L spectrometer (60 MHz). MS spectra were measured with a Finnigan-4021 spectrometer.

The phase transition temperatures of the target compounds were measured by optical microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Mettler FP-80) and control unit (FP-82), and by differential scanning calorimetry (DSC, Shimidazu DSC-50 calorimeter with a data system, heating and cooling rate 5°C min^{-1}). The transition temperatures reported in this article were the peak values of the transition on DSC traces. Phase identification was made by comparing the observed textures with those reported in the literature.

Synthesis

All of the obtained liquid crystals were purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl acetate (20/1) as eluent and then recrystallized from acetone/methanol.

Typical synthetic process: to a mixture of compound 4-*n*-octoxyphenylacetylene (0.44 mmol), compound **1** (0.4 mmol), bis(triphenylphosphine)palladium dichloride (20 mg), triphenylphosphine (60 mg), and CuI (60 mg), under dry N_2, was added 20 mL of anhydrous triethylamine. The obtained mixture was heated under reflux under stirring for 2 h. Analysis by TLC revealed completion of the reaction. The precipitate formed was then filtered off and washed with ether. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane as eluent. The obtained compound was recrystallized from acetone/methanol. Compound **A**: $[\alpha]_D{}^{20} = -1.60$ (25°C, $CHCl_3$). Mp 49.5°C. IR (KBr) υ_{max}: 2925, 2854, 2217, 1727, 1604, 1511, 1467, 1210, 1168, 833 cm^{-1}. ^1H NMR δ_H (60 MHz; $CDCl_3$; TMS): 0.88–1.90(m, 31H, aliphatic hydrogens), 3.96(t, J = 6 Hz, 2 H), 4.30–4.50(m, H), 6.70–7.55(m, 10H, ArH), 8.05(d, J = 8 Hz, 2 H, ArH) ppm. MS m/z (rel. int.): 554(M^+, 1.69), 233($C_8H_{17}OC_6H_4CO^+$, 43.70), 121($HOC_6H_4CO^+$, 100.00). Elemental analysis: calculated ($C_{37}H_{46}O_4$), C, 80.11; H, 8.36%; found, C, 79.62; H, 8.23%.

Compound **B**: $[\alpha]_D^{20} = -6.91$ (25°C, $CHCl_3$). Mp 25.0°C. IR (KBr) υ_{max}: 2929, 1734, 1603, 1510, 1492, 1207, 1167, 990 cm^{-1}. ^1H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.88–1.90(m, 31 H, aliphatic hydrogens), 4.20–4.50(m, 3 H), 6.80–8.17(m, 8 H, ArH) ppm. ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 61.10(d, J = 18.8 Hz, 2 F), 80.20(d, J = 18.8 Hz, 2F) ppm. MS m/z (rel. int.): 627($M^+ + 1$, 1.28), 233($C_8H_{17}OC_6H_4CO^+$, 100.00), 121($HOC_6H_4CO^+$, 96.44). Elemental analysis: calculated ($C_{37}H_{42}F_4O_4$), C, 70.91; H, 6.75; F, 12.13%; found, C, 70.87; H, 6.94; F, 11.95%.

Compound **C**: $[\alpha]_D^{20} = -2.45$ (25°C, $CHCl_3$). Mp 77.1°C. IR (KBr) υ_{max}: 2928, 2856, 2217, 1729, 1618, 1514, 1467, 1204, 1165, 838 cm^{-1}. ^1H NMR δ_H (60 MHz; $CDCl_3$; TMS): 0.85–2.00(m, 31H, aliphatic hydrogens), 4.02(t, J = 6 Hz, 2 H), 4.70(q, J = 6 HZ, H), 6.75–7.60(m, 9 H, ArH), 8.17–8.53(m, 2 H, ArH) ppm. MS m/z (rel. int.): 600($M^+ + 1$, 5.65), 166($HO(NO_2)C_6H_3CO^+$, 100.00). Elemental analysis: calculated ($C_{37}H_{45}NO_6$), C, 74.10; H, 7.56; N, 2.33%; found, C, 73.54; H, 7.72; N, 1.86%.

Compound **D**: IR (KBr) υ_{max}: 2929, 2857, 1740, 1612, 1510, 1492, 1204, 1168, 990 cm^{-1}. ^1H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.88–1.90(m, 31 H, aliphatic hydrogens), 4.20–4.70(m, 3 H), 7.10–8.60(m, 7 H, ArH) ppm. ^{19}F NMR δ_F(56.4 MHz, $CDCl_3$, TFA): 61.10(d, J = 18.8 Hz, 2F), 80.20(d, J = 18.8 Hz, 2 F) ppm. MS m/z (rel. int.): 672($M^+ + 1$, 1.80), 166($HO(NO_2)C_6H_3CO^+$, 100.00).

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